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XIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON TERNARY MIXTURES.

FIRST PAPER.

By Wilder D. Bancroft.

Presented by C. L. Jackson, May 9, 1894.

Following out the analogy between dissolved substances and gases, Nernst deduces the law that, when two dissolved substances have no common ion and do not react chemically, the influence of each on the solubility of the other is zero, within certain undefined limits. He says:* "Die Analogie zwischen der Auflösung und Sublimation bezw. Dissociation fester Stoffe zeigt sich nun auch deutlich ausgesprochen, was den Einfluss fremden Zusatzes betrifft. Ebenso wenig wie die Sublimationsspannung bei Gegenwart fremder indifferenter Gase sich ändert, wird die Loslichkeit eines festen Stoffes durch Zusatz eines zweiten (in nicht zu grosser Menge) beeinflusst, wofern der hinzugefügte fremde Stoff nicht chemisch auf jenen einwirkt; und ebenso wie die Dissociationsspannung im höchsten Maasse durch Zusatz eines der gasförmigen Zersetzungsproducte beeinflusst wird, so variirt entsprechend auch die Löslichkeit derjenigen Stoffe, bei welchen die Auflösung mit einem mehr oder weniger vollständigen Zerfall verbunden ist, die also bei ihrer Auflösung mehrere Molekülgattungen liefern, wenn eine dieser letzteren der Lösung hinzugefügt wird." There are several things in this statement which are open to criticism. If taken literally, the author implies a fundamental difference between solutions of liquids in liquids, and solids in liquids, a distinction which is not in accordance with the view that in dilute solutions the solute,† whether liquid or solid in the pure state, behaves like a gas at that temperature. If applied to any dissolved substance, the statement just quoted is too inaccurate to need any comment. The precipitation of salts by alcohol is a well known instance where it does not apply, and, in general, adding to a solution a substance in which the solute is practically insoluble diminishes the solubility of the latter. This is recognized by Nernst, for he has based a method for determining reacting weights upon it.* Even if limited to solids, the proposition cannot be admitted. We have the precipitation of lactones by potassium carbonate as an intermediate step, and the precipitation of salts by phenol as a definite case of diminished solubility without the presence of a common ion. Other cases could be cited, if necessary, and there are also examples where an increase of solubility takes place when a solid substance is added to a solution containing another solid as solute. The explanation usually offered under these circumstances is, that "double molecules" are formed, a mode of getting round the facts which is not always entirely satisfactory.

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* Theor. Chemie, p. 383.

† There seems to me a need for a word denoting the dissolved substance. In future I shall use the word "solute," meaning the substance dissolved in the solvent. Instead of the phrase "infinitely miscible liquids," I propose "consolute" liquids.

Since in the application of the gas laws to solutions there has been observed no difference between a solid and a liquid when dissolved, I am inclined to think that the general statement should be, that in all cases where a third substance, *B*, is added to a solution of *A* in *S*, the solubility of *A* undergoes a change. This variation may be large or small, positive or negative, depending on the nature of the three substances *A*, *B*, and *S*. When both *A* and *B* are liquids, or even when only one of them is, the effect is so marked as to be familiar to all; when both are solids, the effect is not yet recognized by so competent an authority as Nernst.

The work of the last few years on solutions has been devoted to bringing out the analogy between the dissolved substance and gases. In the cases of changed solubility, no common ion being present, the analogy is no longer with gases, but with liquids. The added substance acts as a liquid, precipitating the solute more or less in proportion as the dissolved substance happens to be more or less soluble in it. The laws governing these displacements are entirely unknown, with the exception of Nernst's Distribution Law,† which is only a first approximation, in that it takes no account of the changing mutual solubilities of the hypothetically non-miscible liquids. Under these circumstances it seemed to me desirable to investigate the laws governing systems composed of three substances, and the experiments which I communicate in this paper have been made on the simplest form of ternary mixtures, that where all three substances are liquids. The subject has been very little studied, the only researches known to me being by Tuchschmidt and Follenius,[*] Berthelot and Jungfleisch,[†] Duclaux, [‡] Nernst, [§] and Pfeiffer. [‖] Of these, all except the first and last deal with the equilibrium between two liquid phases; the paper of Tuchschmidt and Follenius contains but one series of measurements, while Pfeiffer remarks, apropos of his own extended investigations, that "there is very little to be made out of them." In this he does himself an injustice, for, as I shall show, his results are very satisfactory and astonishingly accurate when one remembers how they were made.

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* Zeitschr. f. ph. Chem., VI. 16. 1890.

† Teilingssatz.

The simplest case of three-liquid systems is when one has two practically non-miscible liquids, and a third with which each of the others is miscible in all proportions; for then any complication due to the mutual solubility of the two dissolved liquids is avoided. It is possible to say something *a priori* about the law which governs these saturated solutions. Let A and B be two non-miscible liquids, S the common solvent with which A and B are miscible in all proportions when taken singly, and let the quantity of S remain constant, so that we are considering the amounts of A and B, namely x and y, which will dissolve simultaneously in a fixed amount of S. It is known, experimentally, that the presence of A decreases the solubility of B, and *vice versa;* it is required to find the law governing this change of solubility. This, being a case of equilibrium, must come under the general equation of equilibrium.

$$\text{(1)} \qquad \frac{\delta F(x, y)}{\delta x} dx + \frac{\delta F(x, y)}{\delta y} dy = 0,$$

where dx and dy denote the changes in the concentrations of A and B respectively.

This equation, though absolutely accurate, is of no value practically so long as the differential coefficients are unknown functions. In regard to them we may make two assumptions. The decrease in the solubility of A may be proportional to the amount of B added, and independent of the amounts of A and B already present in the solution. The differential equation expressing this is:

$$\text{(2)} \qquad a\,dx + b\;y = 0,$$

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[*] B. B., IV. 583. 1871.

[†] Ann. chim. phys., [4.], XXVI. 396. 1872.

[‡] Ibid., [5.], p. 264. 1876.

[§] Zeitschr. f. ph. Chem., VI. 16. 1890.

[‖] Ibid., IX. 469. 1892.

where a and b are proportionality factors and constants. This equation may be rejected on *a priori* grounds, because it does not show that when B is absent, the miscibility of A with S is infinite, and also because it has no similarity with the other equations representing chemical equilibrium. The second assumption is that the change in solubility may be a function of the amounts of A and B already present. This is the usual condition of chemical equilibrium, and is known as the Mass Law. Its mathematical expression is

$$\frac{\alpha\, dx}{x} + \frac{\beta\, dy}{y} = 0, \text{ or}$$

$$\alpha\, d \log x + \beta\, d \log y = 0, \tag{3}$$

where x and y denote the amounts of A and B in a constant quantity of S, α and β are proportionality factors, and the logarithms are natural logarithms.

If α and β are constants, this equation is integrable, and gives when cleared of logarithms:

$$x^{\alpha}\, y^{\beta} = \text{Constant.} \tag{4}$$

If we make $\frac{\alpha}{\beta} = n$, we shall have:

$$x^{n}\, y = C, \tag{5}$$

where C is of course different in value from the constant in equation (4).

Before we proceed to test equation (5) experimentally, it remains to be seen in what unit x and y should be expressed. It is obvious that the nature of the unit has no effect on the general form of the equation, nor upon the exponential factor n. The only change will be in the value of the integration constant log C, so that the measurements may be expressed in any form that is convenient, as chemical units,* for example, grams per litre, volumes, reacting volumes, or anything else. It is not even necessary that x and y be expressed in the same unit, though it would probably always be more practical. In my own experiments x and y are expressed in cubic centimeters because they were measured directly as such, and in this way it was not necessary to make determinations of the densities of the liquids used, nor any assumptions in regard to their reacting weights. Equation (5) will not remain unchanged if the reacting weight of A or B varies, that is, if the ratio of the active mass to the actual mass changes as x or y changes. The converse of this is also true, that if the system follows the law $x^n y = C$, the common solvent remaining constant, the reacting weights of the substances A and B cannot have varied with the concentration.

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* I have adopted the following nomenclature for molecular and atomic weights, viz. reacting and combining weights. As the reacting weight is proportional to the chemical unit experimentally, I propose that the gram molecule in the unit of volume (reacting weight in grams per litre) be called the chemical unit, or simply the unit. The object of these arbitrary changes in our chemical terms is to do away with everything involving or implying the assumption of the existence of molecules and atoms.

I have found that the equation, $x^\alpha y^\beta =$ Constant, is the expression representing the saturated solutions of two non-miscible liquids in a constant quantity of a consolute liquid. I find, however, that in most cases the concentrations cannot be given by one curve, but involve two, so that for one set of concentrations I have the relation $x^{n_1} y = C_1$, for the other set $x^{n_2} y = C_2$. This cannot be true unless the two sets of saturated solutions correspond to different conditions. This is the case. Duclaux* found that a saturated solution of amylalcohol and water in ethylalcohol became turbid on adding a drop either of amylalcohol or of water. In other words the solution was sensitive to an excess of either liquid.† I have confirmed this result, and it is perfectly general. It is not proper, however, to draw the conclusion that the solution is saturated in respect to both liquids. If to a given saturated solution of chloroform, water, and alcohol, for instance, one adds a drop of water or of chloroform, the solution becomes turbid; but what separates out is the same in both cases. It is analogous to a saturated solution of salt in a mixture of alcohol and water. It is indifferent whether one adds alcohol or salt to the solution. In either case, there is a precipitate; but in both cases the precipitate is salt, and the solution is saturated in respect to salt, not in respect to alcohol. It is not so easy to see what takes place in a system composed of liquids because the precipitate, being itself a liquid, dissolves part of the solution, and the new phase is not composed of pure substance. This need not trouble us, for, theoretically at any rate, the precipitate may be treated as pure liquid, and the final equilibrium looked upon as due to a subsequent reaction. One of the two curves represents, then, the set of solutions which is saturated in respect to chloroform, and not in respect to water. Whether one adds water or chloroform, to these solutions, the precipitate is chloroform. The other curve represents the mixtures which are saturated in respect to water, and not in respect to chloroform. Either water or chloroform, when added to these solutions, produces a precipitate of water. These two sets of solutions are easily distinguishable qualitatively, because in the first case the new phase, containing a large percentage of chloroform, is denser than the mixture from which it separates, while in the second case the new phase, containing chiefly water, is lighter than the original solution. The point where the new phase changes from being denser to being lighter than the first phase is the point of intersection of the two curves. At this point only is the nature of the precipitate determined by the nature of the infinitely small excess added. The intersecting point represents the concentration at which, were chloroform and water solids at that temperature, both could be in equilibrium with the solution and its saturated vapor. It corresponds to the concentration of a solution containing two salts with a common ion which is in equilibrium with the two solid salts, formation of a double salt being excluded. In one respect the analogy between a system having three liquid components and one composed of two solids and a liquid does not hold. If to a saturated solution of silver bromate silver acetate is added, the precipitate is silver bromate, and, conversely, the precipitate is silver acetate if silver bromate be added to a saturated solution of silver acetate. The salt with the less concentration precipitates the one with the greater, up to a certain point. In a chloroform-water-alcohol mixture in which chloroform is present in large quantities, the precipitate is water, or the substance with the greater precipitates the one with the lesser concentration. This difference of behavior is due to the new phase being a solid in the one case and a liquid in the other. By a suitable choice of the three components, and by varying the temperature, the substance in respect to which the solution was saturated could be made to separate either as a liquid or a solid phase, and this difference could be made zero. The transition point would come when the equilibrium was between four phases, one solid, two liquid, and one gaseous.

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* Ann. chim. phys, [5.], VII. 264. 1876.

† Ostwald, Lehrbuch, I. 819.

There is no apparent theoretical reason why the two curves should not be prolonged beyond their intersection ; but there is a very good practical one. Beyond the point of intersection the curves denote saturated but labile solutions, and a supersaturated system composed of liquids is almost impossible to realize. When I come to the study of ternary mixtures having one or more solid components, I hope to be able to follow one of the curves at least beyond the intersecting point; but in the present work I have made no such attempt.

I will now describe the method used in my work, and then take up the experimental data obtained. As pairs of non-miscible liquids, I have taken chloroform and water, benzol and water; and as consolute liquids, ethylalcohol, methylalcohol, and acetone. The next point was how to determine the composition of the saturated solutions. The methods of quantitative analysis are useless in this case; but the problem is solved without difficulty by quantitative synthesis. Instead of making a saturated solution and analyzing it, I measured the quantities required to make a saturated solution at the required temperature. Definite amounts of the consolute liquids were put in test tubes by means of a carefully graduated pipette; varying quantities of one of the non-miscible liquids were run in from a burette, and the second non-miscible liquid added from another burette to saturation. The test tubes were corked, warmed just above the temperature at which the final readings were made, so that there should be a single homogeneous liquid layer, and placed in a constant temperature bath. If the tube clouds, it is beyond the saturation point; if it remains clear, it is not up to it, the required value lying between the two. By making a series of experiments one can bring the limiting values very close together, and thus determine the saturation point with great accuracy. The constant temperature bath was at 20° C. No correction was made for the amounts of the three liquids evaporating off into the vapor space in the upper part of the test tubes; but by using different sized test tubes this space did not vary much, being about five cubic centimeters, so that the error due to this may be neglected.

The chloroform used (Squibb's) was treated with sodium bisulphite solution to free it from acetone, washed thoroughly with water, dried over calcium chloride and fractionated, twelve hundred grams going over within one quarter of a degree. Kahlbaum's crystallized benzol was recrystallized twice and fractionated to constant boiling point. The ethylalcohol was dried over lime and copper sulphate and fractionated. The lot used distilled within half a degree. Part of the acetone (from Eimer and Amend) was converted into the bisulphite compound, back again, dried over potassium carbonate and calcium chloride, and fractionated. Another portion was treated direct with calcium chloride and fractionated. I could detect no difference between the two lots. I tried to purify a sample of acetone from Cutler Brothers, purporting to be manufactured by Merck in Darmstadt; but it was so bad that I used none of it in my experiments. The methylalcohol (from Kahlbaum) was dried over anhydrous copper sulphate and fractionated.

The measurements in the tables are the mean of at least four determinations, and the error is probably not more than 5% except in the cases where the quantity of one component is less than 0.20 c.c., when it may easily rise to 10%. The values for n are accurate to within 2% without much question. The values for log C are more untrustworthy, being much affected by a slight variation in n, while the term C is liable to even greater fluctuations, and is not given, as being too uncertain. Under the headings "Calc." are the values required by the formula to correspond with the experimental data for the other component. The figures in the column marked log C are Briggsian logarithms. As will be noticed, I have not always taken the mathematical mean of this column as the value of log C in the formula. It seemed better to take the value which best satisfied the experimental data, and to ignore numbers which were obviously faulty.

TABLE I.

x c.c. H_2O; y c.c. $CHCl_3$; 5 c.c. Alcohol. Temp. 20°.

Formula $x^{n_1} y = C_1$; $n_1 = 1.90$; log $C_1 = 1.190$.

Water.		$CHCl_3$		
Calc.	Found.	Calc.	Found.	log C_1.
9.94	10.00	0.195	0.20–	1.195
8.99	9.00	0.24	0.24	1.192
7.98	8.00	0.30	0.30	1.193
7.14	7.00	0.385	0.37	1.174
6.00	6.00	0.515	0.515	1.190
5.00	5.00	0.73	0.73	1.191
3.97	4.00	1.12	1.13	1.197
			Average,	1.190

Formula $x y^{n_2} = C_2$; $n_2 = 1.111$; log $C_2 = 0.742$.

				log C_2.
3.00	3.00	1.78	1.73	0.741
1.99	2.00	2.49	2.51	0.745
1.01	1.00	4.66	4.60	0.737
0.92	0.91	5.07	5.00	0.736
0.755	0.76	5.96	6.00	0.745
0.635	0.63	7.06	7.00	0.738
0.55	0.55	8.00	8.00	0.743
0.48	0.49	8.86	9.00	0.750
0.43–	0.425	10.06	10.00	0.739
0.20	0.20–	20.00	20.00	0.742
0.127	0.125	30.24	30.00	0.738
			Average,	0.741

TABLE II.

x c.c. Water; y c.c. $CHCl_3$; 5 c.c. Methyl Alcohol. Temp. 20°.
Formula $x^{n_1} y = C_1$; $n_1 = 2.30$; $\log C_1 = 1.291$.

Water.		$CHCl_3$.		
Calc.	Found.	Calc.	Found.	log C_1.
9.91	10.00	0.10	0.10	1.300
5.01	5.00	0.48	0.48	1.288
4.03	4.00	0.81	0.80	1.283
1.99	2.00	3.97	4.00	1.294
			Average,	1.291

Formula $x^{n_2} y = C_2$; $n_2 = 1.25$; $\log C_2 = 1.061$.

				log C_2.
1.49	1.49	7.00	7.00	1.061
1.34	1.35	7.93	8.00	1.065
1.12	1.12	10.00	10.00	1.061
			Average,	1.062

TABLE III.

x c.c. Water; y c.c. Chloroform; 5 c.c. Acetone. Temp. 20°.
Formula $x^{n_1} y = C_1$; $n_1 = 1.415$; $\log C_1 = 0.194$.

Water.		Chloroform.		
Calc.	Found.	Calc.	Found.	log C.
5.01	5.00	0.16	0.16	0.193
4.00	4.00	0.22	0.22	0.194
3.47	3.50	0.266	0.27	0.201
3.00	3.00	0.33	0.33	0.193
2.49	2.50	0.43	0.43	0.196
2.01	2.00	0.586	0.58	0.189
			Average,	0.194
	1.50		0.74	
	1.20		0.83	
	1.00		0.955	
	0.93		1.00	
	0.79		1.12	
	0.71		1.20	
	0.58		1.40	
	0.53		1.50	
	0.505		1.60	
	0.38		2.00	
	0.30–		2.50	
	0.25		3.00	
	0.21		3.50	
	0.19		4.00	
	0.16		5.00	
	0.12		10.00	

TABLE IV.

x c.c. Water; y c.c. Benzol; 5 c.c. Alcohol. Temp. 20°.

Formula $x^n y = C$; $n = 1.60$; $\log C = 0.554$.

Water.		Benzol.		
Calc.	Found.	Calc.	Found.	log C.
19.87	20.00	0.03	0.03	0.557
10.65	10.00	0.09	0.08	0.503
7.94	8.00	0.13	0.13	0.559
4.97	5.00	0.273	0.275	0.557
4.00	4.00	0.39	0.39	0.554
3.02	3.00	0.61	0.61	0.558
2.01	2.00	1.18	1.17	0.550
1.72	1.72	1.50	1.50	0.553
1.50	1.50	1.87	1.87	0.554
1.44	1.45	1.98	2.00	0.559
1.00	1.00	3.58	3.57	0.553
0.605	0.605	8.00	8.00	0.554
0.526	0.525	10.04	10.00	0.552
0.34	0.34	20.14	20.00	0.551
			Average,	0.551

TABLE V.

x c.c. Water; y c.c. Benzol; 5 c.c. Methyl Alcohol. Temp. 20°.

Formula $x^{n_1} y = C_1$; $n_1 = 1.48$; $\log C_1 = 0.216$.

Water.		Benzol.		
Calc.	Found.	Calc.	Found.	log C_1.
5.05	5.00	0.15	0.15	0.211
3.95	4.00	0.21	0.215	0.223
3.01	3.00	0.32	0.32	0.211
2.00	2.00	0.59	0.59	0.216
1.40	1.40	1.00	1.00	0.216
			Average,	0.215

Formula $x^{n_2} y = C_2$; $n_2 = 2.00$; $\log C_2 = 0.281$.

				log C_2.
1.13	1.13	1.50	1.50	0.282
1.00	1.00	1.91	1.90	0.279
0.80	0.80	2.99	3.00	0.283
0.69	0.69	4.01	4.00	0.280
0.49	0.49	7.96	8.00	0.283
			Average,	0.281

TABLE VI.

x c.c. Water; y c.c. Benzol; 5 c.c. Acetone. Temp. 20°.
Formula $x^{n_1} y = C_1$; $n_1 = 1.40$; $\log C_1 = 0.262$.

Water.		Benzol.		
Calc.	Found.	Calc.	Found.	log C_1.
7.97	8.00	0.10	0.10	0.264
7.00	7.00	0.12	0.12	0.262
5.04	5.00	0.19	0.19	0.258
4.03	4.00	0.26	0.26	0.258
2.99	3.00	0.393	0.395	0.264
2.49	2.50	0.51	0.51	0.265
2.18	2.20	0.61	0.615	0.269
2.01	2.00	0.69	0.69	0.260
			Average,	0.2625

Formula $x y^{n_2} = C_2$; $n_2 = 1.35$; $\log C_2 = 0.114$.

				log C_2.
1.67	1.67	0.833	0.833	0.114
1.50	1.50	0.90	0.90	0.114
1.30	1.30	1.00	1.00	0.114
1.005	1.00	1.215	1.21	0.112
0.65	0.65	1.67	1.67	0.114
0.51	0.51	2.00	2.00	0.114
0.38	0.38	2.49	2.50	0.116
0.295	0.295	3.00	3.00	0.114
0.20	0.20	4.00	4.00	0.114
0.15	0.15	4.96	5.00	0.119
			Average,	0.1145

There is but one exception, in the chloroform-water-acetone series. As chloroform and water behave normally with alcohol (Table I.), water and acetone with benzol (Table VI.), the disturbing effect must be due to chloroform and acetone in presence of each other. I have not yet had time to investigate mixtures of chloroform and acetone in the absence of water, to determine whether they are abnormal in respect to any other physical properties. In the other five cases the agreement between observed and calculated values is a remarkable one, well within the limits of experimental error, and this in spite of the wide range that the measurements cover. In the benzol-water-alcohol series the ratio of benzol to water varies as one to forty thousand; in the chloroform-water-alcohol series the ratio chloroform-water varies as one to twelve thousand. In the last measurement of Table I. the chloroform forms over 85% by volume synthetically of the solution, so that in this instance we are well beyond the realms of the "dilute solutions," without noticing any disturbing effect due to "variations from the gas laws." The series benzol-water-alcohol is represented by a single curve; but it must not be thought that in this it forms a real exception to the other mixtures. Theoretically, there are two curves for this series; but the two happen to have the same direction, and therefore appear as one. The point where the precipitate ceases to be less dense than the original solution lies between the mixtures benzol 2.00 c.c., water 1.45 c.c., and benzol 3.57 c.c., water 1.00 c.c.

The formula $x^\alpha y^\beta =$ Constant is not satisfactory, because it contains no term expressing the variation of the consolute liquid in case one of the non-miscible liquids is kept constant, and also because a change in the units in which x and y are expressed or a change in the amount of the consolute liquid taken affects the constant of the formula. This can be remedied by the following reasoning. According to Gibbs and to experiment, the absolute mass of a phase has no effect on the equilibrium. Therefore increasing the quantities of x and y m-fold involves increasing the quantity of the consolute liquid m-fold if the solutions are to remain at the saturation point. This would increase the value of the constant $m^{x+\beta}$ times. If then x and y denote the values in cubic centimeters of the non-miscible liquids A and B, z the corresponding value for the consolute liquid S, we have as equation of equilibrium for saturated solutions the expression:

$$\text{I.} \qquad \frac{x^\alpha y^\beta}{z^{\alpha+\beta}} = C.$$

If, as was done, z is kept constant, this simplifies to formula (4), which I will renumber Ia.

$$\text{Ia.} \qquad x^\alpha y^\beta = C_1.$$

If y is constant, x and z varying, we have:

$$\text{Ib.} \qquad \frac{x^\alpha}{z^{\alpha+\beta}} = C_2.$$

And if x is constant, y and z varying, we have:

$$\text{Ic.} \qquad \frac{y^\beta}{z^{\alpha+\beta}} = C_3.$$

In equation I the value of C is a function of the nature of the units in which x, y, and z are expressed; but independent of the size. Thus grams and kilograms give the same result, cubic centimeters and litres; but the weight constant is different from the volume constant, and the constants for reacting weights or reacting volumes would have still other values. C is also dependent on the absolute value of the exponential factors a and β. We can however eliminate this effect by writing

$$(6) \qquad C = K^{a+\beta},$$

in which case K remains entirely unchanged, when we substitute $\frac{a}{\beta} = n$. In Table VII. I give in the first two columns the values for log C according to the general formula $\frac{x^n y}{z^{n+1}} = C$, when x, y, and z are expressed in volumes. Since $z = 5$ in all these measurements, Table VII. gives the constants of the preceding tables less the corresponding values of $(n+1)$ log 5. It would have been better to calculate the integration constant using the rational exponents a and β; but only their ratio can be determined by a study of equilibrium in one liquid layer, and the case of two liquid layers will form the subject of a separate communication. In columns three and four are the corresponding values of K_1 and K_2 according to equation (6). They are the constants of the preceding two columns divided by the appropriate values of $n + 1$.

TABLE VII.

Mixtures.	log C_1.	log C_2.	log K_1.	log K_2.
H_2O, $CHCl_3$, C_2H_5OH	$\bar{1}.163$	$\bar{1}.266$	$\bar{1}.711$	$\bar{1}.652$
H_2O, $CHCl_3$, CH_3OH	$\bar{2}.984$	$\bar{1}.489$	$\bar{1}.692$	$\bar{1}.773$
H_2O, $CHCl_3$, CH_3COCH_3	$\bar{2}.506$	....	$\bar{1}.381$	....
H_2O, C_6H_6, C_2H_5OH	$\bar{2}.737$	$\bar{2}.737$	$\bar{1}.514$	$\bar{1}.514$
H_2O, C_6H_6, CH_3OH	$\bar{2}.482$	$\bar{2}.184$	$\bar{1}.388$	$\bar{1}.395$
H_2O, C_6H_6, CH_3COCH_3	$\bar{2}.584$	$\bar{2}.471$	$\bar{1}.410$	$\bar{1}.349$

The values given under x and y in Tables I.–VI. are amounts of the liquids A and B in a given quantity of S, — in this case 5 c.c. A glance at the tables will show that these figures are very far from expressing volume concentrations, i. e. quantity of substance in a given volume of the solution. As most theoretical generalizations in chemistry are expressed in volume concentrations, it will be necessary to see what effect such a change would have on general Formula I. If there is no contraction or expansion on mixing, the volume of the solution will be the sum of the component volumes, or $V = x + y + z$, and the volume concentrations will be $\frac{x}{x+y+z}$, $\frac{y}{x+y+z}$, $\frac{z}{x+y+z}$, respectively. This simple case may be said never to occur, and the volume of the solution is an at present unknown function of the component volumes represented by the expression $V = F(x, y, z)$. While the knowledge of the form of this function is necessary to enable us to calculate the volume concentrations of a given solution from our experimental data, it is superfluous in the present discussion. We have (from Formula I.):

$$\alpha \log x + \beta \log y - (\alpha + \beta) \log z = \log C.$$

Now $$\alpha \log V + \beta \log V - (\alpha + \beta) \log V = 0;$$

$$\therefore \quad \alpha \log \frac{x}{V} + \beta \log \frac{y}{V} - (\alpha + \beta) \log \frac{z}{V} = \log C;$$

or $\dfrac{x^\alpha y^\beta}{z^{\alpha+\beta}} = C$, if x, y, and z denote volume concentrations instead of having their previous significance. Since α, β, and C remain unchanged, we find that Equation I represents the series of saturated solutions obtained at constant temperature with any two non-miscible liquids, and a third liquid miscible in all proportions with each of the other two, provided no chemical reaction takes place and provided the reacting weights of the liquids remain unchanged. It is immaterial whether x, y, and z denote volume concentrations, or concentrations of two of the substances in a constant quantity of the third.

As has been said, volume concentrations are generally looked upon as the only scientific way of expressing data. This is perfectly natural when we remember that our theoretical ideas have been formed almost entirely upon a study of the gaseous state. It is not a necessary method, and in this particular case it is decidedly disadvantageous practically to use volume concentrations. It involves a determination of the density of each solution, increasing the work and bringing in a new source of error. When expressed in volume concentrations all three components vary, and while it is a simple matter to plot three variables in a plane,* I know of no way in which this can be done for the logarithms of these variables. By the method which I have followed, one constituent can be kept constant, no density determinations are necessary, and there are only two variables. The formula being hyperbolic, by plotting the data on logarithmic co-ordinates one gets a straight line, any variation from which is easily seen, while the constants of the curve can be determined from the diagram with more speed and accuracy than by substituting the experimental values in an equation and solving for two unknown quantities.

The next case to be considered is when we have two partially miscible liquids, and a third miscible in all proportions with each of the others. Formula I cannot apply here, because it was deduced for two non-miscible liquids, and this condition is no longer fulfilled. There are two ways of treating a problem like this. One is to change the conditions of the experiment until they agree with the formula. The other is to change the formula till it conforms to the conditions of the experiment. I have done both. I will suppose, for the sake of clearness, that the two partially miscible liquids are ether and water. Saturated solutions of water in ether are absolutely non-miscible at the temperature for which they are saturated, being thus an improvement over benzol and water, which are slightly miscible theoretically. If x and y in equation Ia mean quantities of saturated water and saturated ether solutions, instead of pure water and pure ether, the conditions are satisfied for which this formula was deduced, and the equation must apply. I have found that it did, and the experimental proof is given in Tables IX. and XI.

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* Gibbs, Thermodynamische Studien, p. 141; Roozeboom, Zeitschr. f. ph. Chem., XII. 369, 1893.

This being settled, we can attack the second part of the problem. Let X denote cubic centimeters of saturated solution of ether in water, Y cubic centimeters of saturated solution of water in ether which saturate a given quantity of a consolute liquid. It is found experimentally that

$$X^{\alpha} Y^{\beta} = \text{Constant}, \tag{7}$$

or, if we set $\frac{\alpha}{\beta} = n$, we shall have

$$X^{n} Y = C. \tag{8}$$

If s_1 is the solubility of ether in water, s_2 the solubility of water in ether, both expressed in volumes per cubic centimeter of the solvent synthetically, we shall have, if no contraction or expansion takes place in forming the saturated solutions of water in ether and ether in water:

$$X = A + s_1 A; \quad Y = B + s_2 B; \tag{9}$$

$$(A + s_1 A)^{n} (B + s_2 B) = C; \tag{10}$$

where A = c.c. water in X, B_2 = c.c. ether in Y. As we must assume some contraction or expansion, let the ratio of the actual volume to the sum of the component volumes be σ_1 in the saturated solution of ether in water, and σ_2 in the saturated solution of water in ether. We have then:

$$X = \sigma_1 (A + s_1 A); \quad Y = \sigma_2 (B + s_2 B); \tag{11}$$

$$\{\sigma_1 (A + s_1 A)\}^{n} \{\sigma_2 (B + s_2 B)\} = C_1; \tag{12}$$

which can be rewritten:

$$(13) \qquad (A + s_1 A)^n (B + s_2 B) = \frac{C_1}{\sigma_1{}^n \sigma_2}.$$

If x and y denote cubic centimeters of pure water and pure ether dissolved in a given quantity of the consolute liquid, we have:

$$(14) \qquad x = A + s_2 B; \quad y = B + s_1 A.$$

Solving for A and B: —

$$(15) \qquad A = \frac{x - s_2 y}{1 - s_1 s_2}; \quad B = \frac{y - s_1 x}{1 - s_1 s_2}.$$

Substituting these values in (13): —

$$(16) \quad \left\{\frac{1 + s_1}{1 - s_1 s_2}(x - s_2 y)\right\}^n \left\{\frac{1 + s_2}{1 - s_1 s_2}(y - s_1 x)\right\} = \frac{C_1}{\sigma_1{}^n \sigma_2}.$$

Since σ_1, σ_2, s_1, s_2, are constants for constant temperature, we can simplify equation (16) into:

$$(17) \qquad (x - s_2 y)^n (y - s_1 x) = C_2,$$

where the relation between C_1 and C_2 is

$$(18) \qquad \frac{C_1}{C_2} = \frac{\sigma_1{}^n \sigma_2 (1 + s_1)^n (1 + s_2)}{(1 - s_1 s_2)^{n+1}}.$$

Eliminating the effect due to the arbitrary quantity of consolute liquid used, we have:

$$(19) \qquad \frac{(x - s_2 y)^n (y - s_1 x)}{z^{n+1}} = C_3;$$

where $C_3 = \frac{C_2}{z^{n+1}}$. Reverting to the most general form, so as to make the equation correspond in form to Equation I.,

$$\text{II.} \qquad \frac{(x - s_2 y)^\alpha (y - s_1 x)^\beta}{z^{\alpha + \beta}} = C.$$

Equation II. is more general than Equation I., the latter being merely a special case of the former, where the terms representing the mutual solubilities are so small that they can be neglected.

In testing these equations I took, as pairs of partially miscible liquids, ether and water, ethylacetate and water. The ether was distilled over sodium, the ethylacetate dried with calcium chloride and fractionated, the boiling point rising a full degree for a litre distilled off. I think however that no essential error was introduced in this way, and that, for my purposes, it was sufficiently pure. The solubilities were determined volumetrically. In all cases I took 10 c.c. of the solvent in a test tube and ran in the solute from a burette till the solution clouded. One can determine this point to 0.01 c.c. without difficulty. In Table VIII. I give the solubilities at 20° expressed in cubic centimeters of solute in ten cubic centimeters of solvent. The solubilities of ether and ethylacetate in water decrease with increasing temperature; the solubilities of water in ether and ethylacetate increase with increasing temperature. This behavior is well known for ether; but I have not found it stated anywhere for ethylacetate.

TABLE VIII.

Solute	Solvent.	Solubility.
Ether	Water	1.03–4 *
Water	Ether	0.08
Ethylacetate	Water	0.926
Water	Ethylacetate	0.294

It will be remembered that, when two liquids were practically non-miscible, the series of saturated solutions formed by these with a consolute liquid were expressed by two curves of the same general form, but having different constants; and it was found that these two curves represented, the one the series of solutions out of which liquid *B* is precipitated on addition of either *A* or *B*; the other, the converse series, when the solution was saturated in respect to *A* but sensitive to an excess of either *A* or *B*. When the liquids *A* and *B* are partially miscible, the case becomes apparently more complicated, for we have four curves instead of two. These refer to four distinct sets of equilibrium, there being the following four series of saturated solutions.

1. The solution is saturated in respect to *B*. Excess of *A* produces no precipitate.
2. The solution is saturated in respect to *B*. Excess of *A* or *B* produces a precipitate of *B*.
3. The solution is saturated in respect to *A*. Excess of *A* or *B* produces a precipitate of *A*.
4. The solution is saturated in respect to *A*. Excess of *B* produces no precipitate.

Series 2 and 3 correspond to the two series observed with two non-miscible liquids. In these two series the consolute liquid is the solvent, whereas in series 1 and 4 we have, in addition, *A* and *B* respectively as solvents. In Tables IX.–XIII. I give the measurements made with ether and water, ethylacetate and water with the consolute liquids alcohol, methylalcohol, and acetone. In Tables IX. and XI. the experiments were made with saturated solutions; in Tables X., XII., and XIII., with pure liquids. The first method has the advantage that the readings obtained are final, involving no correction and no knowledge of the mutual solubilities. On the other hand, it is necessary to keep the solutions in the burettes at the same temperature as that at which one makes the determinations, a very difficult thing to do usually, so that the second method is to be preferred. The exponential factors are the same according to both methods, as I have already shown. The integration constants are different, standing to each other in the relation given in Equation (18). It would have been well if I had determined the densities of the saturated solutions so that they could be recalculated into cubic centimeters of the pure liquids; but I shall have to make an extended series of density determinations in connection with the equilibrium between two liquid phases, and I have postponed these others till then. The measurements in Tables IX.–XIII. are about as accurate as those in Tables I.–VI., with the exception of the solutions when water is part solvent. The precipitate in these cases is lighter than the solution, consists of a few drops only, and is very difficult to distinguish from air bubbles, especially in the ether solutions, where the clouding at best is very slight. For this reason the first series in each table must be considered as very doubtful as the absolute measurements go. The determination of the saturation point for these cases depended on the light, the state of my eyes, and the mood which I happened to be in on the days when the measurements were made. So difficult are the determinations sometimes, that I give no results for ether-water-acetone because I obtained different measurements every day. The agreement between the observed and the theoretical values is no test of the absolute accuracy of either; but merely shows that the solutions follow the same general law, the constants, exponential, and integration varying with the degree of cloudiness which the observer takes as denoting the point of saturation. The values of n are not so accurate as in the first set of tables, because the curves cover a more limited extent, and therefore the variations are smaller, and because when the value of n is large, say over 2, a very slight change in the direction of the logarithmic curve produces a very large corresponding change in n. The amounts of ethylacetate and water which dissolve in 5 c.c. of alcohol, methylalcohol, or acetone were so large that I was forced to work with one cubic centimeter of these liquids as solvent.

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* Schuncke finds 1.04–5, Zeitschr. f. ph. Chem., XIV. 334. 1894.

TABLE IX.

X c.c. Sat. Water; Y c.c. Sat. Ether; 5 c.c. Alcohol. Temp. 20°.

Formula $XY^{n_1} = C_1$; $n_1 = 2.60$; $\log C_1 = 1.994$.

Sat. Water.		Sat. Ether.		
Calc.	Found.	Calc.	Found.	log C_1.
49.89	50.00	1.30	1.30	1.995
24.89	25.00	1.70	1.70	1.996
10.02	10.00	2.41	2.41	1.993
			Average,	1.995

Formula $X^{n_2}Y = C_2$; $n_2 = 1.49$; $\log C_2 = 1.867$.

				log C_2.
9.04	9.00	2.79	2.77	1.864
7.96	8.00	3.33	3.35	1.870
7.72	7.70	3.52	3.50	1.865
6.00	6.00	5.10	5.10	1.867
			Average,	1.867

Formula $XY = C_3$; $\log C_3 = 1.493$.

				log C_3.
5.19	5.21	5.97	6.00	1.495
4.45	4.45	7.00	7.00	1.493
3.99	4.00	7.78	7.80	1.494
3.89	3.87	8.03	8.00	1.491
3.11	3.10	10.05	10.00	1.491
2.08	2.08	14.95	15.00	1.495
1.78	1.77	17.58	17.50	1.491
			Average,	1.493

Formula $X^{n_4}Y = C_4$; $n_4 = 1.73$; $\log C_4 = 1.665$.

				log C_4.
1.62	1.61	20.28	20.00	1.661
1.43	1.43	24.95	25.00	1.673
1.09	1.10	39.27	40.00	1.666
0.96	0.95	50.47	50.00	1.659
			Average,	1.665

TABLE X.

x c.c. Water; y c.c. Ether; 1 c.c. Methyl Alcohol. Temp. 20°.

Formula $(x - 0.008y)(y - 0.103x)^{n_1} = C_1$; $n_1 = 1.50$; $\log C_1 = \bar{1}.502$.

Water.		Ether.		
Calc.	Found.	Calc.	Found.	log C_1.
10.05	10.00	1.13	1.13	$\bar{1}.500$
9.00	9.00	1.04	1.04	$\bar{1}.502$
7.03	7.00	0.85	0.85	$\bar{1}.500$
4.97	5.00	0.68	0.68	$\bar{1}.505$
4.00	4.00	0.60	0.60	$\bar{1}.502$
				$\bar{1}.502$

Formula $(x - 0.008\,y)^{n_2}\,(y - 0.103\,x) = C_2$; $n_2 = 1.13$; log $C_2 = \bar{1}.928$.

Water.		Ether.		
Calc.	Found.	Calc.	Found	log C_2.
2.95	3.00	0.555	0.56	$\bar{1}.936$
2.50	2.50	0.56	0.56	$\bar{1}.928$
2.03	2.00	0.60	0.59	$\bar{1}.920$
1.80	1.80	0.63	0.63	$\bar{1}.929$
1.50	1.50	0.70	0.70	$\bar{1}.929$
				$\bar{1}.928$

Formula $(x - 0.008\,y)^{n_3}\,(y - 0.103\,x) = C_3$; $n_3 = 2.04$; log $C_3 = 0.045$.

				log C_3.
1.20	1.20	0.90	0.90	0.047
1.00	1.00	1.23	1.23	0.045
0.90	0.89	1.53	1.50	0.035
0.83	0.83	1.79	1.80	0.047
0.78	0.78	2.00	2.00	0.046
0.64	0.64	3.01	3.00	0.043
0.57	0.57	3.99	4.00	0.047
0.52	0.52	5.00	5.00	0.045
0.47	0.47	6.89	7.00	0.053
				0.045

Formula $(x - 0.008\,y)^{n_4}\,(y - 0.103\,x) = C_4$; $n_4 = 4.4$; log $C_4 = \bar{1}.057$.

				log C_4.
0.44	0.44	10.30	10.00	$\bar{1}.044$
0.45	0.45	11.62	12.00	$\bar{1}.071$
0.45	0.45	15.04	15.00	$\bar{1}.056$
				$\bar{1}.057$

TABLE XI.

X c.c. Sat. Water; Y c.c. Sat. Ethylacetate; 1 c.c. Alcohol. Temp. 20°.

Formula $X\,Y^{n_1} = C_1$; $n_1 = 2.86$; log $C_1 = \bar{1}.280$.

Sat. Water.		Sat. Ethylacetate.		
Calc.	Found.	Calc.	Found.	log C_1.
10.05	10.00	0.25	0.25	$\bar{1}.278$
8.07	8.00	0.27	0.27	$\bar{1}.276$
7.11	7.00	0.28	0.28	$\bar{1}.263$
5.97	6.00	0.30	0.30	$\bar{1}.282$
4.97	5.00	0.32	0.32	1.283
3.94	4.00	0.34	0.35–	$\bar{1}.286$
			Average,	$\bar{1}.278$

Formula $X^{n_2} Y = C_2$; $n_2 = 1.80$; $\log C_2 = 0.549$.

Sat. Water.		Sat. Ethylacetate.		
Calc.	Found.	Calc.	Found.	log C_2.
3.00	3.00	0.49	0.49	0.549
2.50	2.50	0.68	0.68	0.548
2.00	2.00	1.02	1.02	0.550
			Average,	0.549

Formula $X^{n_3} Y = C_3$; $n_3 = 1.36$; $\log C_3 = 0.433$.

				log C_3.
1.45	1.50	1.56	1.59	0.445
1.25	1.25	2.00	2.00	0.433
1.06	1.06	2.51	2.50	0.432
1.00	1.00	2.71	2.72	0.434
0.93	0.92	3.04	3.00	0.428
0.75	0.75	4.00	4.00	0.432
			Average,	0.434

Formula $X^{n_4} Y = C_4$; $n_4 = 1.765$; $\log C_4 = 0.372$.

				log C_4.
0.65	0.65	5.02	5.00	0.369
0.59	0.59	5.98	6.00	0.373
0.54	0.54	7.00	7.00	0.372
0.50	0.50	8.00	8.00	0.372
0.44	0.44	9.96	10.00	0.370
			Average,	0.371

TABLE XII.

x c.c. Water; y c.c. Ethylacetate; 1 c.c. Methyl Alcohol. Temp. 20°.

Formula $(x - 0.029\,y)\,(y - 0.093\,x)^{n_1} = C_1$; $n_1 = 1.20$; $\log C_1 = 0.002$.

Water.		Ethylacetate.		
Calc.	Found.	Calc.	Found.	log C_1.
9.92	10.00	1.08	1.08	0.006
6.96	7.00	0.85	0.85	0.005
5.08	5.00	0.72	0.72	$\bar{1}.995$
3.96	4.00	0.69	0.69	0.006
3.01	3.00	0.68	0.68	0.000
2.51	2.50	0.70	0.70	0.001
			Average,	0.002

Formula $(x - 0.029\,y)^{n_2}\,(y - 0.093\,x) = C_2$; $n_2 = 2.78$; $\log C_2 = 0.631$.

				log. C_2.
2.03	2.00	0.83	0.82	0.637
1.80	1.80	1.04	1.04	0.630
1.72	1.70	1.19	1.15	0.617
1.49	1.50	1.63	1.69	0.644
1.41	1.41	1.99	2.00	0.633
			Average,	0.632

Formula $(x - 0.029\,y)^{n_3}\,(y - 0.093\,x) = C_3\,;\ n_3 = 2.00\,;\ \log C_3 = 0.550.$

Water.		Ethylacetate.		
Calc.	Found.	Calc.	Found.	log. C_3.
1.29	1.29	2.51	2.50	0.549
1.20	1.20	2.99	3.00	0.551
1.07	1.07	4.03	4.00	0.547
1.00	1.00	4.88	4.90	0.552
			Average,	0.550

Formula $(x - 0.029\,y)^{n_4}\,(y - 0.093\,x) = C_4\,;\ n_4 = 7.00\,;\ \log C_4 = 0.078.$

				log C_4.
0.97	0.97	6.00	6.00	0.078
0.98	0.98	7.02	7.00	0.076
1.00	1.00	7.61	8.00	0.100
1.03	1.03	9.98	10.00	0.079
			Average,	0.083

TABLE XIII.

x c.c. Water ; y c.c. Ethylacetate ; 1 c.c. Acetone. Temp. 20°.

Formula $(x - 0.029\,y)\,(y - 0.093\,x)^{n_1} = C_1\,;\ n_1 = 1.54\,;\ \log C_1 = \bar{1}.364.$

Water.		Ethylacetate.		
Calc.	Found.	Calc.	Found.	log C_1.
10.12	10.00	1.02	1.01	$\bar{1}.359$
6.99	7.00	0.76	0.76	$\bar{1}.365$
5.01	5.00	0.60	0.60	$\bar{1}.363$
3.00	3.00	0.47	0.47	$\bar{1}.364$
2.00	2.00	0.43	0.43	$\bar{1}.365$
			Average,	$\bar{1}.363$

Formula $(x - 0.029\,y)^{n_2}\,(y - 0.093\,x) = C_2\,;\ n_3 = 1.16\,;\ \log C_2 = \bar{1}.721.$

				log C_2.
1.50	1.50	0.47	0.47	$\bar{1}.721$
1.00	1.00	0.63	0.63	$\bar{1}.721$
			Average,	$\bar{1}.721$

Formula $(x - 0.029\,y)\,(y - 0.093\,x)^{n_3} = C_3\,;\ n_3 = 1.26\,;\ \log C_3 = \bar{1}.653.$

				log C_3
0.79	0.80	0.74	0.74	$\bar{1}.656$
0.69	0.69	0.80	0.80	$\bar{1}.652$
0.51	0.51	1.00	1.00	$\bar{1}.652$
0.31	0.31	1.50	1.50	$\bar{1}.653$
			Average,	$\bar{1}.653$

Formula $(x - 0.029\,y)^{n_4}\,(y - 0.093\,x) = C_4$; $n_4 = 3.00$; $\log C_4 = \bar{2}.135$.

Water.		Ethylacetate.		
Calc.	Found.	Calc	Found.	log C_4.
0.25	0.25	2.01	2.00	$\bar{2}.134$
0.25–	0.25	2.48	2.50	$\bar{2}.138$
0.286	0.285	3.01	3.00	$\bar{2}.134$
0.29	0.29	5.00	5.00	$\bar{2}.135$
			Average,	$\bar{2}.135$

In this set of tables, as in the first set, the amount of one non-miscible liquid which will dissolve in the consolute liquid decreases as the quantity of the other non-miscible liquid increases. In this case, however, the non-miscible liquids are saturated solutions and it does not follow that the quantity of one pure liquid decreases as the other increases. There comes a point where the rate of increase of one component in the solution in which it is solute is greater than its rate of decrease in the solution in which it is solvent. If we take the general Equation (17),

$$(x - s_2\,y)^n\,(y - s_1\,x) = C_2,$$

it is obvious that as x increases y will first decrease, pass through a minimum, and then increase. If the same equation expressed the two equilibria, the point where y was a minimum would be the point where the solution is no longer sensitive to an excess of x. In general, the equilibrium for this second stage is given by a second equation, and all we can say in our present knowledge is that at the intersection of these two curves y should have a minimum value. This does not seem to hold in Table XII., where the amount of ethylacetate soluble in 1 c.c. methylalcohol in presence of 2.50 c.c. water is more than will dissolve when either three or four cubic centimeters of water are added. I am inclined to attribute this to experimental error, as I do not see how there can be two saturated solutions of the same substance in the same solvent. Such a case would be entirely new, and would involve such consequences that it is not to be assumed on the strength of a variation of two one-hundredths of a cubic centimeter on measurements where the probable error is known to be very large. I propose to repeat these measurements on a larger scale, so as to determine what the facts really are. There are also one or two things in respect to the ether-water-methylalcohol curve which need to be gone into more closely. In Table XIV. I give the values for log C when cleared of the term for z, and the values for log K when the effect of the exponential factor has been eliminated. Both log C and log K are calculated for x, y, and z being expressed in cubic centimeters. A discussion of these values is not possible at present, and in any case they should be reduced to reacting volumes or eacting weights before a rational treatment could be thought of.

TABLE XIV.

Mixtures.	log C_1.	log C_2.	log C_3.	log C_4.	log K_1.	log K_2.	log K_3.	log K_4.
S . H_2O, S. Ether, Alcohol	$\bar{1}.478$	0.126	0.095	$\bar{1}.757$	$\bar{1}.855$	0.051	0.047	$\bar{1}.911$
H_2O, Ether, Methylalcohol	$\bar{1}.502$	$\bar{1}.928$	0.045	$\bar{1}.057$	$\bar{1}.801$	$\bar{1}.966$	0.015	$\bar{1}.825$
S . H_2O, S. Et. Ac., Alcohol	$\bar{1}.280$	0.549	0.433	0.372	$\bar{1}.814$	0.196	0.182	0.134
H_2O, Et. Ac., CH_3OH	0.002	0.631	0.550	0.078	0.001	0.167	0.183	0.001
H_2O, Et. Ac., Acetone	$\bar{1}.364$	$\bar{1}.721$	$\bar{1}.653$	$\bar{2}.135$	$\bar{1}.749$	$\bar{1}.871$	$\bar{1}.894$	$\bar{1}.534$

The measurements already communicated would be sufficent by themselves to establish the general law governing this class of equilibria; but I have in addition experiments by other investigators which give the same result. In 1871 Tuchschmidt and Follenius* noticed that carbon bisulphide was not infinitely miscible with aqueous alcohol and they made a series of experiments to determine the saturation points when carbon bisulphide was added to alcohol of known strengths. They expressed their results by means of a complex empirical formula. This is not necessary, as the general equation for two non-miscible liquids covers the case entirely. In Table XV. the first column gives the number of cubic centimeters of carbon bisulphide which will dissolve in ten cubic centimeters of aqueous alcohol of the percentage composition by weight given in column two. In column three is the strength of alcohol as required by the formula.

TABLE XV.

x = g. H_2O ; y = c.c. CS_2. Temp. 17°.

Formula $x\,y^n = C$; $n = \frac{5}{3}$; log $C = 1.345$.

	% Alcohol.		
y.	Calc.	Found.	log C.
18.20	9.88	9.85	1.457
13.20	9.80	9.815	1.318
10.00	9.70	9.695	1.345
7.00	9.50	9.354	1.456
5.00	9.15	9.137	1.350
3.00	8.43	8.412	1.324
2.00	7.40	7.602	1.310
0.20	....	4.84	....
		Average,	1.366

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* B. B., IV. 583. 1871.

When one considers that the carbon bisulphide was evidently determined very roughly, the agreement is an excellent one. Here, too, we find the existence of two curves. The last measurement lies on the second curve when water is the precipitate, and not carbon bisulphide. As only one point on this curve was measured, it is impossible to determine the constants even approximately. The object of this investigation by Tuchschmidt and Follenius was to obtain a method for determining the strength of aqueous alcohol quickly and easily. Owing to the unpleasant properties of carbon bisulphide, their choice of liquids was bad, though the method seems to me a good one. If one were to make a complete table for benzol or chloroform and aqueous alcohol at zero degrees, the rest would be simplicity itself. One would take ten cubic centimeters of the alcohol to be tested and run in chloroform from a burette till saturated, when a glance at the table would give the percentage composition of the alcohol. The method would be quicker than any except with a hydrometer, and more accurate than that. An idea of the accuracy is given by the fact that at 20°, 5 c.c. of 96% alcohol require about 20 c.c. chloroform, while the same amount of 97.5% alcohol requires about 30 c.c. for saturation. For a weaker alcohol the change for each per cent is much less ; but the measurements can be made more accurately.

I will now take up the measurements of Pfeiffer * on the miscibility of various esters with alcohol and water. The measurements were not made under the most favorable circumstances. A known amount of the ester was poured into a beaker, a definite quantity of alcohol added, and water run in till the saturation point was reached. Nothing was done to prevent evaporation, nothing, so far as is mentioned, to keep a constant temperature, and there was no means of warming the solution above the final temperature in order to insure that equilibrium had been reached. The necessity of this last had already been pointed out by Duclaux,† who found that, on cooling a solution below its saturation point, it clouded at once ; but on warming, the equilibrium was reached much more slowly. Given these untoward conditions, the comparative accuracy of the measurements is remarkable. While Pfeiffer has given us series upon series of valuable measurements, showing the increase of miscibility of esters and water in presence of alcohol, he has curiously enough omitted all determinations of the miscibility of water and esters when no alcohol is present. This is still

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* Zeitschr. f. ph. Chem., IX. 469. 1892.

† Ann. chim. phys., [5.], VII. 264. 1876.

more remarkable if one considers the uselessness of comparing the effect of equal quantities of alcohol on ethylacetate and water, amylacetate and water, without allowing for the fact that ethylacetate is roughly forty times as soluble in water as amylacetate. As these solubilities had to be known at any rate approximately, in order to apply Equation II. to Pfeiffer's experimental data, I have determined several myself. Through the courtesy of Mr. Dunlap of the organic laboratory, I received small quantities of ethylbutyrate, ethylisovalerate, and isoamylacetate. I dried them over calcium chloride and fractionated. The change of boiling point of the portions used was four degrees for the ethylisovalerate and two degrees for each of the others. The amounts at my disposal made it not worth while to attempt further purification. In Table XVI. I give the solubilities in cubic centimeters of the solute in ten cubic centimeters of the solvent at 20°. For purposes of comparison I have also inserted in this table the values for ethylacetate from Table VIII.

TABLE XVI.

Solute.	Solvent.	Solubility.
Ethylacetate	Water	0.926
Water	Ethylacetate	0.294
Isoamylacetate	Water	0.02
Water	Isoamylacetate	0.12
Ethylbutyrate	Water	0.08
Water	Ethylbutyrate	0.04–5
Ethylisovalerate	Water	0.02–
Water	Ethylisovalerate	0.04+

For these four esters I have found that the solubility in water decreases with increasing temperature, while the solubility of water in the ester increases with increasing temperature, both observations being made at 20°. As there is no obvious reason why these four esters should all be abnormal, it is more than likely that this behavior is characteristic of all esters at ordinary temperatures. As it is improbable that the solubility of the esters in water can continue to decrease indefinitely with increasing temperature, there must be some point where it reaches a minimum, and it is quite possible that a determination of this temperature for different esters might give interesting results. The experiments could be made with great ease as the amount of saponification during the time necessary for a measurement would be very small.

Quite recently, de Hemptinne* has determined the solubilities of several esters in water at 25°. His measurements are given in grams of the solute per litre of solution. I have reduced his measurements to cubic centimeters of solute in ten cubic centimeters of solvent by dividing by the densities as far as I could get them out of Landolt and Börnstein's tables and Roscoe and Schorlemmer's text-book, disregarding the difference between a litre of solution and a litre of solvent. The results which I give in Table XVII. are only rough approximations, but quite sufficient for my purpose. The figures in the second column are the densities used in recalculating de Hemptinne's figures.

XVII.

Solute.	Solubility	Density.
Isobutylacetate	0.07	0.88
Amylacetate	0.02–	0.88
Methylbutyrate	0.115	0.94
Ethylbutyrate	0.08–	0.898
Amylbutyrate	0.006	0.85
Propylpropionate	0.06+	0.88
Amylpropionate	0.01+	0.88
Ethylvalerate	0.03	0.86

De Hemptinne did not measure the solubility of water in the esters, and I have not been able to find any data on the subject beyond the few measurements which I have made myself. In considering Pfeiffer's results, this is not very serious, because he worked always with three cubic centimeters of esters, adding alcohol in varying quantities, and water to saturation. As the solubility of water in the different esters can be rarely more than one per cent, the error in calculating the amount of water required to saturate will in no case be more than a tenth of a cubic centimeter, and will rarely exceed two or three hundredths. The solubilities of esters in water, which have not been determined by de Hemptinne or myself, have been filled in as best I could by analogy, remembering that increase of carbon means decrease of solubility, and that among isomeric esters the one with the smaller acid radical was rather the less soluble. In deciding where between two limits an unknown solubility should be put, I have taken the figure which satisfied the experimental data best. The solubilities thus obtained lay no claim to being accurate; but they are not very far out, probably in no case more than 100%, and this rough approximation is better than treating the esters and water as absolutely non-miscible. In Table XVIII. I give the solubilities which I have used in calculating Pfeiffer's results, expressed in cubic centimeters of the ester in ten cubic centimeters of water.

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* Zeitschr. f. ph. Chem., XIII. 561. 1894.

XVIII.

Solute.	Solubility.	Solute.	Solubility.
Methylvalerate	0.20	Propylacetate	0.30
Ethylvalerate	0.03	Butylacetate	0.07
Methylbutyrate	0.12	Amylacetate	0.02
Ethylbutyrate	0.08	Propylformiate	0.40
Propylbutyrate	0.02	Butylformiate	0.10
Ethylpropionate	0.30	Amylformiate	0.05
Propylpropionate	0.065		

Starting, as Pfeiffer did, with a constant quantity of ester, his results necessarily lie almost entirely along the curve representing the equilibrium when addition of water or ester produces a precipitate of ester. In a few cases there are a few measurements, never more than two, on the curve where water or ester produces a precipitate of water. There are not enough of these measurements to enable me to determine the direction of this second curve, and in the tables I have therefore given no calculated values in these cases. The point where, according to Pfeiffer, infinite miscibility occurs is the beginning of the curve where the solution is saturated in regard to ester; but water produces no precipitate. The corresponding curve where the solution is saturated in respect to water, while addition of ester produces no precipitate, did not come within the scope of Pfeiffer's investigations at all. It will be noticed that in the last measurements of each series the amount of water required to saturate is very generally greater than the theoretical quantity. I attribute this variation entirely to experimental error. When one is working with one hundred cubic centimeters of solution or more, it becomes almost impossible to determine the first appearance of clouding with great accuracy. In Tables XIX. to XXXI. I give Pfeiffer's results, with the values for the water calculated according to the formula at the top of each table. It is only fair to Herr Pfeiffer to say that, if I had arranged the exponential factors so that z should have been raised to the first power only, the differences between the observed and the calculated values would have been less than they now are. I felt, however, that, as the water was the thing I was calculating, I would make its exponential factor unity instead of that of the alcohol.

TABLE XIX.

$y = 3$ c.c. Methylvalerate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.02\,x)^{0.37} / z^{1.37} = C$; $\log C = \bar{1}.807$.

	x.		
z.	Calc.	Found.	log C.
3	....	1.66	....
6	5.04	5.06	$\bar{1}.809$
9	8.88	9.03	$\bar{1}.815$
12	13.28	13.40	$\bar{1}.809$
15	18.34	18.41	$\bar{1}.809$
18	23.90	24.00	$\bar{1}.809$
21	30.09	30.09	$\bar{1}.807$
24	36.80	36.72	$\bar{1}.806$
27	44.35	44.15	$\bar{1}.805$
30	52.80	52.37	$\bar{1}.803$
33	62.60	62.25	$\bar{1}.804$
36	74.25	74.15	$\bar{1}.806$
39	91.45	91.45	$\bar{1}.807$
42	....	∞	$\bar{1}.807$

TABLE XX.

$y = 3$ c.c. Ethylvalerate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.003)^{0.40} / z^{1.40} = C$; $\log C = \bar{1}.682$.

	x.		
z.	Calc.	Found.	log C.
3	....	1.42	....
6	3.81	4.14	$\bar{1}.718$
9	6.73	7.18	$\bar{1}.710$
12	10.07	10.51	$\bar{1}.701$
15	13.81	14.13	$\bar{1}.692$
18	17.80	18.09	$\bar{1}.688$
21	22.15	22.40	$\bar{1}.687$
24	26.80	26.83	$\bar{1}.683$
27	31.65	31.70	$\bar{1}.683$
30	36.70	36.62	$\bar{1}.681$
33	42.15	41.81	$\bar{1}.678$
36	47.65	48.00	$\bar{1}.685$
39	53.40	53.13	$\bar{1}.679$
42	59.40	58.35	$\bar{1}.674$
45	65.55	63.60	$\bar{1}.668$
48	71.90	69.97	$\bar{1}.670$
51	78.50	76.90	$\bar{1}.672$
54	83.25	84.25	$\bar{1}.688$
57	92.40	90.53	$\bar{1}.673$
60	99.50	98.60	$\bar{1}.678$

	x.		
z.	Calc.	Found.	log C.
63	106.80	105.20	$\bar{1}.675$
66	114.70	112.80	$\bar{1}.674$
69	122.40	121.90	$\bar{1}.680$
72	130.40	131.00	$\bar{1}.684$
75	138.90	140.20	$\bar{1}.687$
78	148.00	158.70	$\bar{1}.712$
81	157.50	180.00	$\bar{1}.740$
			$\bar{1}.687$

TABLE XXI.

$y = 3$ c.c. Methylbutyrate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x(y - 0.012)^{0.52} / z^{1.52} = C$; log $C = \bar{1}.888$.

	x.		
z.	Calc.	Found.	log C.
3	2.33	2.34	$\bar{1}.889$
6	6.75	6.96	$\bar{1}.902$
9	12.67	12.62	$\bar{1}.886$
12	19.90	19.45	$\bar{1}.878$
15	28.38	28.13	$\bar{1}.884$
18	38.76	38.80	$\bar{1}.889$
21	50.85	55.64	$\bar{1}.927$
24	....	∞	$\bar{1}.892$

TABLE XXII.

$y = 3$ c.c Ethylbutyrate; $x =$ c.c Water; $z =$ c.c. Alcohol.

Formula $(x - 0.005y)(y - 0.008x)^{0.41} / z^{1.41} = C$; log $C = \bar{1}.785$.

	x.		
z.	Calc.	Found.	log C.
3	....	1.66	....
6	4.90	5.00	$\bar{1}.794$
9	8.73	8.81	$\bar{1}.789$
12	13.08	13.10	$\bar{1}.786$
15	17.95	17.82	$\bar{1}.782$
18	23.50	23.25	$\bar{1}.780$
21	29.24	29.04	$\bar{1}.782$
24	35.55	35.16	$\bar{1}.784$
27	42.35	41.75	$\bar{1}.779$
30	49.40	49.05	$\bar{1}.782$
33	57.12	57.00	$\bar{1}.784$
36	65.69	65.73	$\bar{1}.786$
39	75.25	76.02	$\bar{1}.790$
42	84.05	86.58	$\bar{1}.798$
45	94.50	100.57	$(\bar{1}.812)$
48	106.00	115.40	$(\bar{1}.822)$
51	119.50	137.40	$(\bar{1}.846)$
54	....	∞	$\bar{1}.786$

TABLE XXIII.

$y = 3$ c.c. Propylbutyrate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.002\,x)^{0.378} / z^{1.378} = C$; $\log C = \bar{1}.651$.

z.	x.		log C.
	Calc.	Found.	
3	....	1.19	....
6	3.49	3.55	$\bar{1}.658$
9	6.11	6.13	$\bar{1}.652$
12	9.05	9.05	$\bar{1}.651$
15	12.31	12.31	$\bar{1}.651$
18	15.92	15.90	$\bar{1}.650$
21	19.68	19.68	$\bar{1}.651$
24	23.72	23.72	$\bar{1}.651$
27	27.92	27.84	$\bar{1}.650$
30	32.20	32.10	$\bar{1}.649$
33	36.71	36.71	$\bar{1}.651$
36	41.66	41.55	$\bar{1}.650$
39	46.64	46.49	$\bar{1}.649$
42	51.56	51.60	$\bar{1}.652$
45	56.80	56.90	$\bar{1}.652$
48	62.64	62.40	$\bar{1}.649$
51	67.84	68.00	$\bar{1}.652$
54	73.93	73.85	$\bar{1}.650$
			$\bar{1}.651$

TABLE XXIV.

$y = 3$ c.c. Ethylpropionate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.03\,x)^{0.39} / z^{1.39} = C$; log. $C = \bar{1}.931$.

z.	Calc.	Found.	log C.
3	2.36	2.32	$\bar{1}.924$
6	6.89	6.87	$\bar{1}.930$
9	12.38	12.35	$\bar{1}.930$
12	19.10	19.17	$\bar{1}.933$
15	27.12	27.12	$\bar{1}.931$
18	36.84	36.84	$\bar{1}.931$
21	50.35	50.42	$\bar{1}.932$
24	....	∞	$\bar{1}.930$

TABLE XXV.

$y = 3$ c.c. Propylpropionate; $x =$ c.c. Water; $z =$ c c. Alcohol.

Formula $x\,(y - 0.0065\,x)^{0.45} \,/\, z^{1.45} = C$; $\log C = \bar{1}.733$.

	x.		
z.	Calc.	Found.	log C.
3	....	1.58	....
6	4.45	4.70	$\bar{1}.757$
9	8.27	8.35	$\bar{1}.738$
12	12.25	12.54	$\bar{1}.743$
15	17.04	17.15	$\bar{1}.736$
18	22.27	22.27	$\bar{1}.733$
21	28.00	27.83	$\bar{1}.731$
24	34.20	33.75	$\bar{1}.727$
27	40.80	40.24	$\bar{1}.727$
30	47.95	47.15	$\bar{1}.725$
33	55.70	54.65	$\bar{1}.725$
36	63.50	63.18	$\bar{1}.731$
39	72.25	71.59	$\bar{1}.729$
42	81.15	83.05	$\bar{1}.743$
45	91.30	93.91	$\bar{1}.746$
48	102.00	107.46	$\bar{1}.756$
			$\bar{1}.737$

TABLE XXVI.

$y = 3$ c.c. Propylacetate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.03\,x)^{0.23} \,/\, z^{1.23} = C$; $\log C = 0.166$.

	x.		
z.	Calc.	Found.	log C.
3	4.44	4.50	0.170
6	10.57	10.48	0.163
9	17.75	17.80	0.167
12	25.95	26.00	0.167
15	35.72	35.63	0.165
18	46.50	47.50	0.178
21	59.00	58.71	0.164
24	....	∞	0.168

TABLE XXVII.

$y = 3$ c.c. Butylacetate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.007\,x)^{0.3} / z^{1.3} = C$; $\log C = \bar{1}.912$.

	x.		
z.	Calc.	Found.	log C.
3	....	2.08	....
6	6.06	6.08	$\bar{1}.914$
9	10.29	10.46	$\bar{1}.920$
12	15.04	15.37	$\bar{1}.922$
15	20.10	20.42	$\bar{1}.918$
18	25.64	25.60	$\bar{1}.911$
21	31.49	31.49	$\bar{1}.912$
24	37.60	37.48	$\bar{1}.911$
27	44.05	43.75	$\bar{1}.909$
30	50.74	50.74	$\bar{1}.912$
33	58.00	59.97	$\bar{1}.927$
			$\bar{1}.916$

TABLE XXVIII.

$y = 3$ c.c. Amylacetate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.02\,x)^{0.294} / z^{1.294} = C$; $\log C = \bar{1}.861$.

	x.		
z.	Calc.	Found.	log C.
3	....	1.76	....
6	....	4.24	....
9	9.03	9.03	$\bar{1}.861$
12	13.11	13.24	$\bar{1}.866$
15	17.43	17.52	$\bar{1}.864$
18	22.22	22.22	$\bar{1}.861$
21	26 99	26.99	$\bar{1}.861$
24	32.24	32.14	$\bar{1}.860$
27	37.59	37.23	$\bar{1}.856$
30	42.78	42.66	$\bar{1}.859$
33	48.41	48.41	$\bar{1}.861$
			$\bar{1}.861$

TABLE XXIX.

$y = 3$ c.c. Propylformiate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.04\,x)^{0.38} / z^{1.38} = C$; $\log C = \bar{1}.967$.

	x.		
z.	Calc.	Found.	log C.
3	2.82	2.83	$\bar{1}.969$
6	7.52	7.50	$\bar{1}.966$
9	13.65	13.50	$\bar{1}.962$
12	21.30	21.60	$\bar{1}.973$
15	30.95	30.60	$\bar{1}.962$
18	52.40	53.00	$\bar{1}.972$
21	....	∞	$\bar{1}.967$

TABLE XXX.

$y = 3$ c.c. Butylformiate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.01\,x)^{\frac{1}{3}} / z^{\frac{4}{3}} = C$; $\log C = 0.057$.

z.	Calc.	Found.	log C.
3	3.43	3.45	0.060
6	8.71	8.83	0.063
9	15.02	14.75	0.049
12	22.32	21.45	0.041
15	30.25	29.65	0.048
18	39.00	39.00	0.057
21	48.80	51.80	0.083
24	....	∞	0.057

TABLE XXXI.

$y = 3$ c.c. Amylformiate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.005\,x)^{0.35} / z^{1.35} = C$; $\log C = \bar{1}.808$.

	x.		
z.	Calc.	Found.	log C.
3	....	1.80	....
6	4.92	5.17	$\bar{1}.829$
9	8.54	8.77	$\bar{1}.820$
12	12.63	12.64	$\bar{1}.809$
15	17.10	17.01	$\bar{1}.806$
18	21.90	21.86	$\bar{1}.807$
21	27.06	27.06	$\bar{1}.808$
24	32.50	32.31	$\bar{1}.805$
27	38.31	38.31	$\bar{1}.808$

z.	x.		log C.
	Calc.	Found.	
30	44.40	44.50	$\bar{1}.809$
33	50.71	50.71	$\bar{1}.808$
36	57.20	57.82	$\bar{1}.813$
39	62.70	65.21	($\bar{1}.830$)
42	71.35	77.05	($\bar{1}.842$)
45	78.75	85.10	($\bar{1}.842$)
48	86.55	94.20	($\bar{1}.845$)
			$\bar{1}.811$

In addition to these tables, Pfeiffer made a few measurements on amylalcohol, monochlor-, dichlor , and trichloracetic ester in the presence of alcohol and water. The solubility of amylalcohol in water is given by Roscoe and Schorlemmer as two parts in a hundred, and I have used this value. I could find no data whatsoever in regard to the chloracetic esters, so I have calculated the values on the false assumption that they are non-miscible with water. The effect of this error is seen very markedly in the case of the monochloraceticester, which is undoubtedly the most soluble of the three. I give these tables in spite of the known inaccuracy, because the absolute values of the constants are, for the time being, of little value, whereas it is essential to show that the same general law covers all substances and that the substitution of chlorine for hydrogen does not affect the action of the Mass Law. The coincidence of the three choraceticesters having the same exponential factor is probably only superficial, as the correction for the solubilities would alter the exponential factor somewhat.

TABLE XXXII.

$y = 3$ c.c. Amylalcohol; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y = 0.02\,x)^{0.4} / z^{1.4} = C$; log $C = 0.100$. Temp. 9.1°.

z.	x.		log. C.
	Calc.	Found.	
3	3.81	3.21	....
6	10.26	10.35	0.104
9	18.53	18.34	0.095
12	28.45	27.47	0.085
15	40.85	41.25	0.104
			0.097

TABLE XXXIII.

$y = 3$ c.c. Amylalcohol; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.02\,x)^{0.4} / z^{1.4} = C$; $\log C = 0.112$. Temp. 19.2°.

	x.		
z.	Calc.	Found.	$\log C$
3	3.93	3.50	....
6	10.55	10.80	0.122
9	19.10	19.10	0.112
12	30.05	29.15	0.099
15	42.30	43.15	0.121
			0.114

TABLE XXXIV.

$y = 3$ c.c. Monochloraceticester; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,y^{0.43} / z^{1.43} = C$, $\log C = \bar{1}.700$.

	x.		
z.	Calc.	Found.	$\log C$.
3	1.54	1.32	$\bar{1}.644$
6	4.05	4.01	$\bar{1}.695$
9	7.23	7.30	$\bar{1}.705$
12	10.91	10.78	$\bar{1}.695$
15	15.04	16.16	$\bar{1}.731$
18	19.50	22.16	$\bar{1}.756$
21	24.33	28.74	$\bar{1}.772$
			$\bar{1}.714$

TABLE XXXV.

$y = 3$ c.c. Dichloraceticester; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,y^{0.43} / z^{1.43} = C$; $\log C = \bar{1}.479$.

	x.		
z.	Calc.	Found.	$\log C$.
3	0.90	0.90	$\bar{1}.477$
6	2.44	2.45	$\bar{1}.481$
9	4.35	4.33	$\bar{1}.477$
12	6.54	6.60	$\bar{1}.482$
15	9.04	9.20	$\bar{1}.487$
			$\bar{1}.481$

TABLE XXXVI.

$y = 3$ c.c. Trichloraceticester; $x =$ c.c. Water; $z =$ c c. Alcohol.

Formula $x\,y^{0.43} / z^{1.43} = C$; log $C = \bar{1}.336$.

	x.		
z.	Calc.	Found.	log C.
3	0.65	0.65	$\bar{1}.336$
6	1.76	1.80	$\bar{1}.347$
9	3.13	3.02	$\bar{1}.321$
12	4.72	4.50	$\bar{1}.315$
15	6.50	6.50	$\bar{1}.336$
			$\bar{1}.331$

Tables XIX.–XXXI. furnish a striking confirmation of the way in which the Mass Law applies to this class of phenomena; while some of the results are not as satisfactory, perhaps, as I should like, there are some, notably those with propylbutyrate, where the agreement between the observed and the calculated values is something marvellous, though it is unfortunate that the solubility of propylbutyrate in water has never been determined experimentally.

As it might be thought a mere assumption that the first measurements in several series were determinations of another equilibrium, namely, of a saturated solution from which water or ester precipitated water, I have made a few measurements with the few esters I had on hand. The object of these measurements was to show that the change from one equilibrium to another did come at the point shown by Pfeiffer's results, and to make sure that the variations in Pfeiffer's data were due to experimental error. On this account I have made no measurements on the end curves, where water and where ester are part solvents, and in the case of ethylisovalerate I have measured only one series. The results are given in Tables XXXVII.–XXXIX.

TABLE XXXVII.

$x =$ c.c. H_2O; $y =$ c.c. Ethylisovalerate; 5 c.c. Alcohol. Temp 20°.

Formula $(x - 0.004\,y)^n\,(y - 0.002\,x) / z^{n+1} = C$; $n = 2.45$; log $C = \bar{1}.149$.

Water.		Et Val.		
Calc.	Found.	Calc.	Found.	log C.
9.98	10.00	0.15	0.15	$\bar{1}.152$
8.05	8.00	0.24	0.23	$\bar{1}.142$
6.01	6.00	0.46	0.46	$\bar{1}.147$
4.99	5.00	0.72	0.72	$\bar{1}.152$
4.00	4.00	1.23	1.23	$\bar{1}.149$
				$\bar{1}.148$

TABLE XXXVIII.

x = c.c. H_2O; y = c.c Ethylbutyrate; 5 c.c. Alcohol. Temp. 20°.

Formula $(x - 0.005\,y)^{n_1}\,(y - 0.008\,x)\,/\,z^{n_1+1} = C_1$; $n_1 = 2.44$; $\log C_1 = \bar{1}.449$.

x.		y.		
Calc.	Found.	Calc.	Found.	$\log C_1$.
9.99	10.00	0.34	0.34	$\bar{1}.450$
8.01	8.00	0.51	0.51	$\bar{1}.447$
5.97	6.00	0.95	0.96	$\bar{1}.453$
5.01	5.00	1.45	1.44	$\bar{1}.447$
3.99	4.00	2.46	2.47	$\bar{1}.451$
				$\bar{1}.449$

Formula $(x - 0.005\,y)^{n_2}\,(y - 0.008\,x)\,/\,z^{n_2+1} = C_2$; $n_2 = 1.20$, $\log C_2 = \bar{1}.623$.

				$\log C_2$
2.96	2.96	3.99	4.00	$\bar{1}.624$
2.46	2.48	4.94	5.00	$\bar{1}.628$
2.12	2.10	6.07	6.00	$\bar{1}.618$
				$\bar{1}.623$

TABLE XXXIX.

x = c.c. Water; y = c.c. Isoamylacetate; 5 c.c. Alcohol. Temp 20°

Formula $(x - 0.012\,y)^{n_1}\,(y - 0.002\,x)\,/\,z^{n_1+1} = C_1$; $n_1 = 3.50$; $\log C_1 = \bar{1}.414$.

x.		y.		
Calc.	Found.	Calc.	Found.	$\log C_1$.
7.00	7.00	0.41	0.41	$\bar{1}.414$
6.00	6.00	0.70	0.70	$\bar{1}.414$
5.01	5.00	1.32	1.31	$\bar{1}.411$
				$\bar{1}.413$

Formula $(x - 0.012\,y)^{n_2}\,(y - 0.002\,x)\,/\,z^{n_2+1} = C_2$; $n_2 = 1.50$; $\log C_2 = \bar{1}.559$.

				$\log c_2$.
3.62	3.61	3.00	3.00	$\bar{1}.558$
3.00	3.01	3.99	4.00	$\bar{1}.560$
2.60	2.60	5.00	5.00	$\bar{1}.559$
				$\bar{1}.559$

Although Pfeiffer does not say so, his amylacetate and ethylvalerate are unquestionably iso- and not the normal compounds. We can now take up the results given in Tables XXXVII.–XXXIX. and see how satisfactorily they fulfil their object. Ethylbutyrate and amylacetate show the change from one equilibrium to the other at the same point that Pfeiffer found. The ethylbutyrate and ethylisovalerate mixtures are perfectly regular at concentrations beyond those used by Pfeiffer, and the isoamylacetate is normal throughout both in Pfeiffer's work and in mine, so that the variations in Tables XXIX.–XXXI. are due to experimental error. The agreement in results between the two sets is shown in Table XL., where I give in the first column the value of the exponential factor $n + 1$ from the formula

$$(x - s_1 y)\,(y - s_2 x)^n \,/\, z^{n+1} = C,$$

and in the second column the values for the simplified integration constant log K.

TABLE XL.

Ester.		$n + 1$.	log K.
Ethylisovalerate	Pfeiffer	1.40	$\bar{1}.773$
“	W. D. B.	1.41	$\bar{1}.754$
Ethylbutyrate	Pfeiffer	1.41	$\bar{1}.847$
“	W. D. B.	1.41	$\bar{1}.840$
Isoamylacetate	Pfeiffer	1.294	$\bar{1}.893$
“	W. D. B.	1.286	$\bar{1}.870$

As will be seen, the values of $n + 1$ are identical, the values for log K, though very close, are not quite the same. This may be due to inaccuracies in the work, but I am more inclined to attribute it to differences in temperature. It is not known at what temperature Pfeiffer worked, and it would take only a slight difference to account for the variation. In Table XLI. I have tabulated the $n + 1$ values from Pfeiffer's results, together with log C and log K.

TABLE XLI.

Ester.	$n + 1$.	log C.	log K.
Methylisovalerate	1.37	$\bar{1}.807$	$\bar{1}.859$
Ethylisovalerate	1.40	$\bar{1}.682$	$\bar{1}.773$
Ethylisovalerate *	1.41	$\bar{1}.653$	$\bar{1}.754$
Methylbutyrate	1.52	$\bar{1}.888$	$\bar{1}.926$
Ethylbutyrate	1.41	$\bar{1}.785$	$\bar{1}.847$
Ethylbutyrate *	1.41	$\bar{1}.774$	$\bar{1}.840$
Propylbutyrate	1.378	$\bar{1}.651$	$\bar{1}.747$
Ethylpropionate	1.39	$\bar{1}.931$	$\bar{1}.878$
Propylpropionate	1.45	$\bar{1}.733$	$\bar{1}.816$
Ethylacetate *	1.555	....	....
Propylacetate	1.23	0.166	0.135
Butylacetate	1.30	$\bar{1}.912$	$\bar{1}.932$
Isoamylacetate	1.294	$\bar{1}.861$	$\bar{1}.893$
Isoamylacetate *	1.286	$\bar{1}.832$	$\bar{1}.870$
Propylformiate	1.38	$\bar{1}.967$	$\bar{1}.976$
Butylformiate	1.333	0.057	0.043
Isoamylformiate	1.35	$\bar{1}.808$	$\bar{1}.858$

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* My own measurements.

The first thing that strikes one about this table is the way in which so many of the $n + 1$ values approximate to 1.40. Why this should be so is entirely unknown. In the log K values we notice that, for the same acid, increasing the carbon atoms in the alcohol radical diminishes the constant. There is only one exception to this, butylformiate, and here the possible error is very large. It looks also as if the constants might be additive, being made up of one factor for the alcohol and another for the acid radical; but the experimental data is too insufficient to justify this hypothesis. It is very much to be hoped that some one will make a careful series of experiments to settle this point.

Formula II. was deduced for the case when the reacting weights of the substances in equilibrium are not functions of the concentration. The measurements of Pfeiffer and myself show that, with the possible exception of the chloroform-water-acetone series, this condition has been satisfied in all the cases studied, though the experiments extended over a wide range of concentrations. This is in flat contradiction with the determinations of the reacting weights by the boiling-point and freezing-point methods. These methods give accurate results only for very dilute solutions, and even then only for certain solutes in certain solvents. To explain the variations, we are forced to assume "double molecules" in some cases, polymerization with increasing concentration in practically all cases, and "variations from the gas laws." I have brought together a large series of measurements in which there is no sign of any of these things. I see only two possible hypotheses to account for this discrepancy: first, to enunciate a new and most interesting law, to wit, presence of a third substance prevents "polymerization" and "variations from the gas laws"; second, the formula for the change of vapor pressure with the concentration is incorrect. The first hypothesis seems to me out of the question, and there remains only the second. It is a bold thing to question so universally accepted a formula, but I feel convinced that it is not right, and that equal reacting weights of different substances do not produce the same change of vapor pressure. I think that the mistake in the past lay in assuming that the work done in compressing a dissolved substance from the volume V_1 to the volume V_2 by means of a semipermeable piston is equal to $\int p\,dv$ between those limits, irrespective of the nature of solute and solvent. I have already collected some experimental evidence in favor of this view, and I hope before long to be able to establish my point.

The facts brought out in this paper throw light on a research by

Abegg[*] carried out under the direction of Arrhenius. Abegg let alcohol diffuse into a salt solution and found, to his surprise, that the salt, instead of remaining equally divided throughout the liquid, diffused somewhat into the part not yet reached by the alcohol. He concludes that this extraordinary behavior can only be accounted for on the assumption that alcohol increases the osmotic pressure of a dissolved salt. What happens is very simple. When the alcohol has diffused only a little way, one may consider the solution as composed of two parts, one containing a large amount of alcohol, the other very little. The dissolved substance, being in this case less soluble in the first layer than in the second, diffuses into the second only to go back again as the alcohol becomes more evenly divided throughout the liquid. Except that the part containing much alcohol and little water merges insensibly into the part containing much water and little alcohol, and is not in equilibrium with it, the case does not differ from two layers formed by ether and water, where it is well known that the concentration of a third substance is not the same in the two layers. The effect of the alcohol is not, as Abegg assumes, to increase the osmotic pressure of the solute, but to diminish its solubility in that portion of the liquid. If, instead of taking salts which were only slightly soluble in alcohol, Abegg had let water diffuse into water containing in solution some substance very soluble in alcohol, slightly soluble in water, he would have observed the opposite effect, and the dissolved substance would have diffused partially into the layer rich in alcohol.

Another line of reasoning which is not quite defensible is that taken by Wildermann,[†] in his paper, "Ueber cyclische Gleichgewichte." His train of thought is something as follows. Suppose he has a system of three phases, bromine, a solution of bromine in water, and the vapor of bromine and water, it being assumed that the amount of water which dissolves in the bromine can be neglected. He adds to the aqueous solution some substance which does not dissolve in bromine perceptibly, such as potassium bromide or sulphuric acid. The three phases, when in equilibrium, have still the same concentration of liquid bromine and of bromine vapor. Therefore the solubility of the bromine in the liquid cannot have changed. It does change experimentally; therefore, in order to reconcile the reasoning with the facts, he concludes that the apparent change, decrease or increase, is due to chemical action, and that the amount of bromine dissolved as such remains unchanged. This may be true in the special examples studied by Wildermann.* That I cannot say; but it is not true that it is a necessary theoretical conclusion, and there is no proof that it is correct in any case. If, instead of adding potassium bromide, we add to the water some liquid in which bromine is readily soluble, the amount of bromine dissolved will increase without there being any reason to assume chemical action in order to account for it. Bromine is not a good substance to consider, because there are so few liquids soluble in water in which it dissolves without decomposition, and also because we cannot ignore the solubility of the added substance in it. Let us rather treat the case when we have iodine instead of bromine. Suppose we have the system, solid iodine, a solution of iodine in water, and vapor of iodine and water; we add alcohol to the solution. The concentrations of the solid iodine and the iodine vapor will remain practically unchanged; therefore the solubility of iodine in the water, and alcohol should remain unchanged according to Wildermann. As a matter of fact it does change, and I do not see how this variation can be attributed to chemical action unless all solution is defined as chemical action, which begs the question though very possibly true. There may be a radical difference between the action of the alcohol and the action of potassium iodide; but that difference has not been shown. As far as I can see, Wildermann's conclusions require that adding alcohol to a saturated salt solution should have no effect on the concentration of the salt because the equilibrium between the solid salt and its own vapor would remain unchanged.

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[*] Zeitschr. f. ph. Chem., XI. 248. 1893.

[†] Ibid., XI. 407.

Early in this paper I proposed the word "solute" as something distinct from "solvent," and it is necessary for me to justify that distinction. The usual way of looking at binary solutions is to consider them as mixtures, and that it is purely arbitrary which of the two substances we consider as solvent and which as dissolved substance. The following citations will show what the prevailing opinion at the present moment is.

Lothar Meyer, after pointing out that in alcohol-water mixtures it depends on the nature of the semipermeable membrane which substance exerts the osmotic pressure, says: † "Mit der Beschaffenheit der Membran tauschen beide Stoffe die Rollen; es ist daher eine Willkür wenn wir den einen als gelöst, den anderen als das Lösungsmittel bezeichnen." Ostwald is consistent to the bitter end, saying: ‡

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* See Jakovkin, Zeitschr. f. ph. Chem., XIII. 539. 1894.

† Zeitschr. f. ph. Chem., V. 24. 1890.

‡ Ibid., XII. 394. 1893.

"Lösungsmittel ist derjenige Stoff des Gemenges, welcher bei dem betrachteten Vorgange ausgeschieden wird." This view is heroically logical, for it means that, when a salt crystallizes from a saturated solution, the mother liquor consists of water dissolved in the salt.

Nernst's position on the subject is doubtful. He puts solutions under the head of physical mixtures and remarks:* "Die verdünnten Lösingen sind Gemische welche eine Komponente in grossen Ueberschuss zu den übrigen enthalten; erstere bezeichnen wir in diesem Falle als das Lösungsmittel, letztere als gelöste Stoffe." On the other hand, he draws a distinction between freezing out the solvent and crystallizing out the solute.† He does not accept the view that the salt is the solvent in a saturated solution; but he does not suggest in any way that there may be different laws for the solute and the solvent. Planck is very clear and precise; he defines dilute solutions in almost the same words as Nernst, and goes on: ‡ "Bei einer beliebigen Lösung kann jeder Bestandtheil derselben als Lösungsmittel oder als gelöster Stoff aufgefasst werden." This means that in a mixture of two liquids either may be considered as the dissolved substance, and will therefore decrease the partial vapor pressure of the other, and this decrease of the vapor pressure will be greater the greater the concentration of the dissolved substance. This is not in agreement with the facts. A saturated solution of ether in water has the same partial vapor pressures as a solution of water in ether saturated at the same temperature.§ For the moment we will consider ether as the dissolved substance. In the first solution, the volume concentration is roughly 10% ; in the second, about 99% at 20° ; and yet this enormous change of concentration has no effect on the partial vapor pressures. The figures are still more remarkable if we consider solutions of chloroform in water and water in chloroform, when one of the components is present in infinitesimal quantities. We must assume one of two things: either that our present formula for the change of the vapor pressure with the concentration is all wrong, since it does not admit of the vapor pressure of one of the components passing through a minimum; or that there is a difference between solvent and solute, and that each has its own law expressing the change of its vapor pressure with the concentration. This time I prefer the second assumption, with all that it implies. The equations of van 't Hoff and Raoult are the rough statements of the laws for the solvent. The corresponding expressions for the solute have not yet been worked out. The distinction between solvent and solute is very clear in solid solutions of metals in metals. Starting from either of two pure metals a depression of the freezing point is noted when the other is added, the two curves thus formed meeting at the melting point of the eutectic alloy. Here there can be no question that along one curve the first metal is solvent, while on the other it plays the role of solute. In the case of two partially miscible liquids there is also no difficulty in determining which is solvent and which solute. When ether and water are shaken together, the upper layer contains water as dissolved substance, the lower ether. With completely miscible liquids having a maximum (or minimum) vapor pressure at some concentration, such as propylalcohol and water (formic acid and water), it is probable that the change of solvent occurs at the concentration corresponding to the maximum (or minimum) vapor pressure. With such things as ethylalcohol and water, which are infinitely miscible and which show no maximum or minimum vapor pressure, it is impossible at present to say at what concentration alcohol ceases to be the solvent and water assumes that duty. As soon as we have worked out the relation between the concentrations in the solution and in the vapor, I feel certain that we shall find that it requires two curves to express the relation, and not one. The intersection of these curves will be the point where the solvent changes. I look upon my own results with ternary mixtures as very significant in this respect, the change from one curve to another coming at the point where the precipitate or the solvent changed. It is interesting to note that at the point, for instance, where an excess of one of the partially miscible liquids first has no effect, the solubility curve of the dissolved substance has a "break." The possibility of such a case has always been denied except by the upholders of the "hydrate theory."

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* Theoretische Chemie, p. 115.

† Ibid., p. 393.

‡ Grundriss der Thermochemie, p. 131.

§ Wied. Ann., XIV. 219, 1881; Ostwald, Lehrbuch, I. 644.

The effect of temperature on the various equilibria will form the subject of a special paper, and I shall reserve for it the discussion of changes of temperature coefficient at the intersections of two curves, one or two very striking instances of which I have come upon incidentally in my work so far. I hope also to be able to present a paper on equilibrium in two liquid layers, a subject which is of especial interest because the theoretical treatment based on the experimental work in this paper gives results which are not in accordance with the assumptions on which Nernst bases his Distribution Law. Besides, there is the application of the Mass Law to the case where one or more of the components is solid, and to the instances where there is an increase instead of a decrease of solubility.

The results of this paper may be summarized briefly as follows.

1. The equilibria between two partially miscible liquids, and a consolute liquid follow the Mass Law.

2. There are four sets of equilibria corresponding to four different series of solutions.

3. If the two liquids are practically non-miscible, there are only two sets of equilibria.

4. The reacting weights of the liquids studied were not functions of the concentration, — possibly with one exception.

5. There is a fundamental difference between the solute and the solvent.

6. The solubility curve of a substance in a varying mixture of two liquids at constant temperature has a break.